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Furan derivatives dynamic in rye bread processing

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Abstract

Furan in food was detected at the beginning of the 21 century. The presence of furans was described in many groups of foodstuffs, for example, in processed fruits and vegetables as well as in canned meat products. Published data about furans underwent a remarkable increase after the development of Solid Phase Micro Extraction (SPME) techniques. The use of SPME coupled with Gas Chromatograph and Mass Spectrometer (GC/MS) allowed determining furan as well in headspace and inside the same sample. In 2004 the European Food Safety Authority (EFSA) published a report of furan content in food from EU member states for evaluating its safety in consumer health. The EFSA has no such information on Latvian foodstuffs. The amount of furan derivatives was measured in several tens. They are formed during thermal food production processes such as: baking, frying, roasting, and cooking. These volatile, aromatic compounds endow food products with their characteristic aroma and taste. The aim of this study was to detect furan volatile derivates change in Latvian rye bread crust and crumb during baking. The SPME coupled with GC-MS technique was used for furan derivatives detection in baked rye bread samples. In this study, 5 furan derivatives were formed during baking in the rye bread crumb, and 9 furan derivatives in the rye bread crust. The formation of furan derivatives was a very dynamic process. The amount of 2-Furancarboxaldehyde sharply increased during baking, reaching the maximum at 45 minutes of baking, then decreased quickly by the end of baking. The amount of volatile furan derivatives was measured according to IS (Internal Standard – 1,2 -dichlorobenzene) The remaining derived furans retained their formation tendency in bread crumb, though at the end of baking this amount was small in comparison with applied internal standard. Four furan derivatives were detected in the rye bread crust, but not in the bread crumb.

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Keywords: furan derivatives; rye bread; baking

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1. Introduction

Furan is a volatile cyclic compound consisting of five members of the four CH groups and one oxygen atom. Furan is the simplest compound of the furan derivatives used in the chemical industry, and sometimes occurs in food products. Furans as well as a large proportion of volatiles form during Maillard reaction, sugar caramelization-thermal treatment in food proceeding.

The IARC has evaluated furans as a possible carcinogen of the 2B group [1]. Based on studies conducted in laboratories with animals at high doses of furan, it is assumed that furan can contribute to the incidence of cancer through long-term exposure to very low levels of furan in foods.

In May 2004, the FDA reported the presence of furan in heat processed baby foods sold in jars and cans, as well as in coffee and other products. Furan content in these products was in the range 2.2-112 µg kg^{-1} [2]. This has led to increased interest in the furan and its derivatives worldwide. Gas chromatography makes it possible to detect more and more new flavour compounds– from 50 compounds 70 years ago to more than 800 compounds at the turn of this century. Furan compounds in heat–treated products can be found in the J.A. Maga study which gathered data on their occurrences in food, their sensory properties and their formation pathways [3].

Similar to the US FDA, the European Food Safety Authority founded an evaluation group and during 2004-2009 collected data from EU Member States for furan content in food [4]. Scientific report data were collected on 2908 furan containing samples from 20 different food categories. The average content of furan in beer and fruit juice was 6 µg kg -1, and in roasted coffee beans was 2.3 µg kg^{-1}. The furan content was lower in ground coffee with an average of 1.1 µg kg-1 and in instant coffee with an average of 589 µg kg^{-1} [5]. Six Member States reported for furan content in grain products. There is no such information from Latvia. Austria, Germany and Ireland reported for 96 furan-containing cereal product samples out of the total 99, and Lithuania, Italy and Finland reported for one sample. The maximum of furan content in grain products was 168 µg kg^{-1}, but the average value was significantly lower at 10-14 µg kg-1.

The adult exposure to furan in EU Member States varied from 0.29 to 1.17 µg/kg b. w. per day [5].The EFSA evaluation group gathered available information for furan on methods of analysis, occurrence, formation, exposure, toxicity, and concluded that the available information was not representative of true picture of furans in food. It is not possible to assess food safety and make any recommendations for changes in dietary regime. Further data and research are needed [4].

The furan formation mechanism is not yet sufficiently investigated. Its formation at pyrolytic conditions was studied in simple model systems. The main precursors of furans are amino acids and reducing sugars which participate in Maillard reaction, oxidation of polyunsaturated fatty acids, carotenoids and ascorbic acid derivatives [6, 7, 8]. Furan content was higher in natural ascorbic acid systems and it rapidly decreased in the presence of other compounds such as sugars, amino acids and lipids. Different precursor combinations reduced furan formation [9].

The FDA recommended HS-GC/MS methodology for furan determination [10], where furans were analyzed as volatile compounds. The method represented a new approach to the rapid characterization of food products. High resolution mass spectrometry allowed information to be gathered on molecular ion origin, creating a permanent database of the product compounds from the volatile part of sample composition [11]. Temperature, equilibrium time and the vial size were key parameters to be optimized for each food [12, 13].

The aim of the present study was to investigate formation of furan and its derivatives in Latvian whole-grain rye bread crust and crumb during baking.

2. Materials & Methods

The samples used in this experiment were obtained from rye whole-grain flour (stock company 'Jelgavas Dzirnavas, Latvia).The dough was made with scald, natural starter and sugar, salt, malt and cumin. The whole-meal rye bread was baked in a Latvian commercial bakery in a wood-fired oven. Four 1 kg loaves were formed and placed in a prebaking oven for 1 minute at a temperature of 400 °C. The loaves were then placed for baking in a chamber oven at a temperature of 250 °C. One loaf was used for measuring temperature during baking of loaf crust surface and crumb temperature inside the loaf by using thermo-couple. The start temperature of crumb was 37 °C and crust start temperature was 61°C. Characteristics of the samples are given in table 1.

Table 1. Characteristics of analysed samples

Rye bread loaf	Baking time [min]	Temperature of crust [°C]	Temperature of crumb [°C]
Nr. 1	30	145	88
Nr. 2	45	152	99
Nr. 3	60	156	100
Nr. 4	75	186	100

After baking, the loaves were left to cool at room temperature for 12 hours. For analysis crust was very carefully separated from the crumb by using a conventional knife. The separated crust and crumb were placed in polypropylene bags and tightly sealed. After 3 days of storage at room temperature the samples were put in cold storage at minus 18 ºC until analysis.

The Solid Phase Micro extraction, Gas Chromatograph and Mass Spectrometer were used for furan derivatives detection in the samples. For SPME 50 g of sample was placed into a 250 ml head space vial. Sample was sampled by using SPME fiber coated with Carboxen/Polydimethylsiloxane (CAR/PDMS), thickness 75 µm. The fiber was manually exposed to the sample headspace for 30 minutes at temperature of 60ºC. Temperature of injection port of GC was 200ºC, desorption time was 1 minute. GC coupled with mass spectrometer (QP2010, Shimadzu) equipped with ZB-WAX Plus capillary column (30.0 m length, 0. 25 mm internal diameter, 0.25 µm film thickness). Injection was in splitless mode.

Helium flow was 0.91 mL min^{-1}. Oven temperature programme was as follows: 40ºC for 5 min, increased at 5ºC/min to 220ºC (2 min). Interface temperature was 200ºC. Ion source temperature was 200ºC. Mass acquisition range was from 38 to 200 m/z. Volatile compounds identification was based on comparison with reference spectra from libraries (Wiley7N2, NIST147, and PAL600K). The relative concentrations of individual compounds were determined by dividing the peak area of every compound by the internal standard's peak area.

The experiment was carried out in the Research Laboratory of Department of Biotechnology, Microbiology and Food Valuation, Warsaw University of Life Sciences in 2010.

3. Results & Discussion

Nine furan derivatives were identified in Latvian baked rye bread by using SPME fibre coated with CAR/PDMS. Most of them have appropriate classification number of Chemical Abstract Service (CAS) and EU Flavour Information System number (FL): 1) 2-Furancarboxaldehyde (CAS 98-01-1; FL 13.018); 2) Ethanone, 1-(2-furanyl)- (CAS 1192-62-7); 3) 2-Furancarboxaldehyde, 5-methyl- (CAS 620-02-0; FL 13.001); 4) 2-Furanmethanol (CAS 98-00-0; FL 13.019); 5) 2-Furancarboxaldehyde, 5-(hydroxymethyl)-

(CAS 67-47-0; FL 13.139); 6) Furan, 2-pentyl- (CAS 3777-69-3); 7) 2-Furanmethanol, acetate (CAS 623-17-6); 8) 1-(2-Furanyl)-2-hydroxyethanone; 9) 5-Formyl-2-furfurylmethanoate.

Furan derivatives attach characteristic odour and taste for bread but the question of their impact on food safety remains unresolved.

The furan derivative 2- Furancarboxaldehyde, 5-(hydroxymethyl) - which is also known by the synonym 5-(Hydrohymethyl)-2-furfuraldehyde (5-HMF) appeared as toxic in animal studies [14, 15]. EFSA for food safety assessment has recommended the Maximised Survey-derived Daily Intake (MSDI) of 0.012 µg/capita/day [16], and modified Theoretical Added Maximum Daily Intake (mTAMDI) to 1600 µg/person/day [17]. The threshold of concern - 540 µg/person/day - relates to food containing 5HMF [18].

Formation of furan derivatives in rye bread crumb during baking is shown in Figure 1.

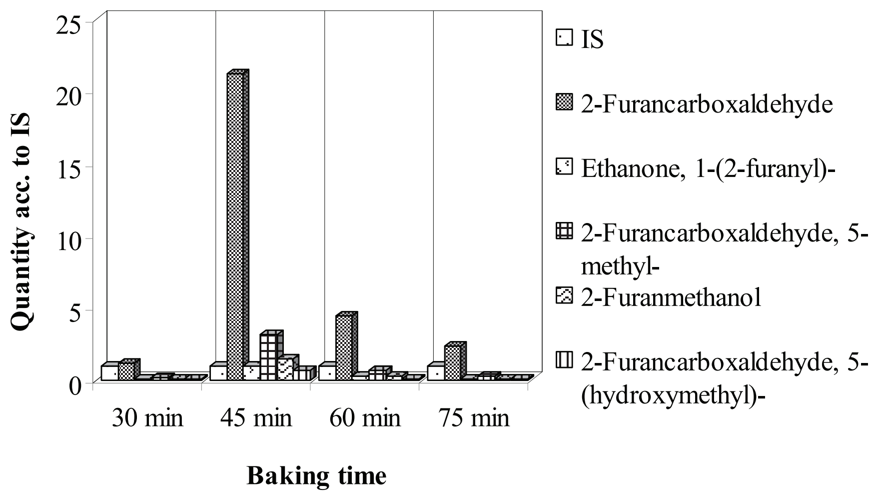

Fig. 1. Furan derivatives in rye bread crumb during baking

The presence of furans has been ascertained in rye bread crumb already at 30 minutes of baking. Rapid formation of 2-Furancarboxaldehyde (furfural) was observed in the subsequent baking stage, and at 45 minutes at a temperature of 99 ºC reached maximum value in comparison with IS. The furfural amount in the next 15 minutes of baking decreases dramatically, and continues to decline after the optimal baking time of 60 minutes. In 1993, Silwar and Lullmann observed a similar dynamic in the process of green coffee roasting where furfural fully formed after 5 minutes at 230 ºC, then fell rapidly, and decomposed at a higher temperature. In 1963 Smith found that furfural forms from the oxidation of furfuryl alcohol and is also formed by decomposition of pentosans, for instance by dehydration of arabinose. In 1991 Mottram showed that furfural is formed from the Amadori compound of a pentose and an intermediate 3-deoxyosone. Furfural is characterized by a sweet, fruit, cherry, soft almond bouquet of odours. In 1967 Arctander described furfural as a pungent, but sweet, bread-like, caramelic, cinnamon-almond-like odour of poor tenacity [19].

In this study it was observed that 2-Furancarboxaldehyde, 5-methyl- formation is taking place at an early stage of the baking process, reaching a maximum at 45 minutes of baking at 98 ºC, then decreases until the end of baking. In 1969 Fagerson described that 2-Furancarboxaldehyde, 5-methyl-forms in the thermal degradation of glucose, Mottram in 1991 has shown that it is formed from the Amadori compound of a hexose and an intermediate 3-deoxyosone.The odour was described as sweet-spicy, warm, and slightly caramelic by Arctander in1967 [19].

Other derivatives - 2-Furanmethanol, Ethanone, 1-(2-furanyl) and 5-HMF in rye bread crumb formed in negligible quantities at the early stage of baking with maximum reached at 45 minutes, than decreases until the end of baking.

The formation of furan derivatives in rye bread crust at different baking times is shown in Figure 2.

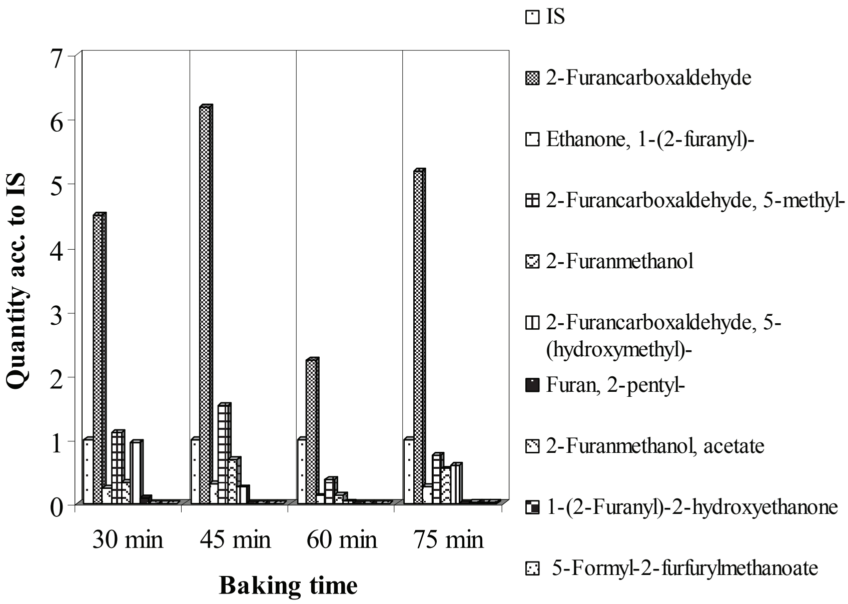

Fig. 2. Furan derivatives in rye bread crust during baking

During baking, temperature increases rapidly in bread crust to higher than 100 ºC. Nine furan derivatives were found in rye bread crust, four derivatives more than in rye bread crumb. In addition to the crumb, identified derivatives Furan, 2-pentyl-, 2-Furanmethanol, acetate, 1-(2-Furanyl)-2-hydroxyethanone, 5-Formyl-2-furfurylmethanoate were detected in more quantity in rye bread crust.

Comparing the formation of furfural in rye bread crumb and crust, it is seen that the amounts at 45 minutes of baking are significantly different. According to IS, furfural in rye bread crumb is 21 and 6 in rye bread crust. The optimal baking time of this rye bread is 60 minutes, and the study showed that the temperature of crumb was 100 ºC, and the temperature of crust was 156 °C - amount of furan derivatives in this time was smallest.

As the baking time increased, the amount of furfural continued to decline in the crumb but in the crust resumed growth. This could be explained by the thermal dehydration process in crust where polysaccharides were present, which was not the case in crumb because polysaccharides were more resistant to involvement in Maillard reaction than mono- and disaccharides [20]. The other furan derivatives appearing in rye bread crust were in negligible amounts, although they form the Latvian rye bread bouquet, determining its quality and excellent taste. This is an important indicator for the consumer to consider in a broad bread market. Attention should be given to 5HMF due to its potentially adverse effects on food safety. From this point of view it would be desirable to determine the content of 5HMF in Latvian rye bread, although the study showed that its maximum of 0.95 according to IS (internal standard), formed at early stage of baking is relatively small. The amount of 5HMF was 0.03 at the optimal baking time of 60 minutes but increased with prolonged baking time to 0.6 at 75 minutes of baking.

4. Conclusions

- Nine volatile furan derivatives were identified in Latvian rye bread- 5 in bread crumb and 9 in bread crust.
- Majority of the volatile furan derivatives form at the early stage of baking, and further reduce during baking.
- During baking the 2-Furancarboxaldehyde, 5-methyl-(5HMF) formed in negligible amounts in Latvian rye bread crust but increased with prolonged baking time.

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